A Versatile Approach to Alcohol, Aldehyde, Ketone and Amine Derivatives Starting from β-Allyl *C*-Glycosides of D-Ribofuranose and 2-Deoxy-D-ribofuranose

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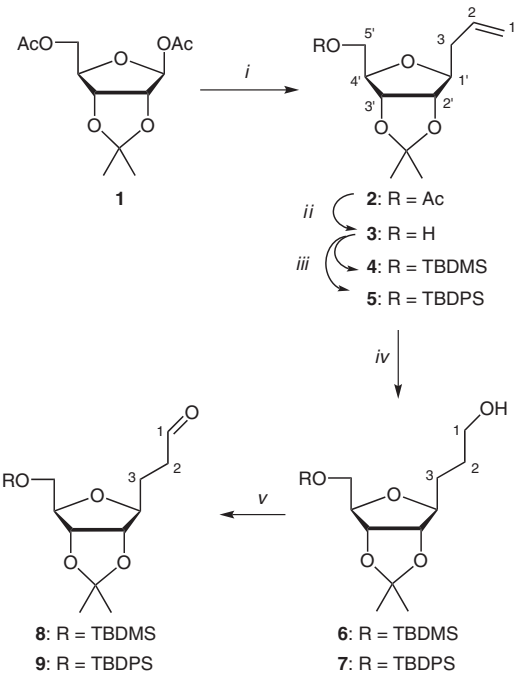
Dedicated to Professor Dr. Rainer Beckert on the occasion of his 60th birthday

Abstract: An efficient preparative procedure is described, leading from β-allyl *C*-glycosides of D-ribofuranose to alcohols by a hydroboration–oxidation procedure. The corresponding aldehydes were obtained by Swern or Dess–Martin oxidation. Alternatively, two of the alcohols were mesylated to gain access to azides and amines. Treatment of the aldehydes with ethynylmagnesium bromide or phenylethynyllithium and consecutive oxidation of the diastereomeric alcohols provided the acetylenic ketones in good to excellent yields. The obtained derivatives serve as important intermediates for the synthesis of various heterocyclic systems.

Key words: ribofuranose, C-nucleosides, hydroboration, oxidation, amines, aldehydes, alkynes

As part of an ongoing research programme that focuses on C-nucleosides, we described recently the first safe, short, and efficient synthetic route to peracetylated β-allyl C-glycosides of D-ribofuranose and 2-deoxy-D-ribofuranose. At present, the best pathway to prepare a β-allyl C-glycoside of D-ribofuranose proceeds via the 2,3-*O*-isopropylidene diacetate **1**[1–3] by treatment with allyltrimethylsilane (AllTMS) and zinc bromide in nitromethane as solvent (Scheme 1).[4,5] Here, we report the synthesis of a series of products, for example alcohols, amines, aldehydes, and acetylenic ketones that are potentially useful for the preparation of a broad range of nucleoside analogues. In view of the diverse application of C-nucleosides, we wished to develop a versatile synthetic route to these types of compounds. It was decided to attempt this by applying a hydroboration–oxidation procedure. However, initial investigations showed that the ester group of C-glycoside **2** is not stable enough for such reaction conditions. Thus, the acetyl group was replaced by a *tert*-butyldimethylsilyl group (TBDMS) and by a *tert*-butyldiphenylsilyl group (TBDPS), providing compounds **4** and **5**,[5] respectively. Deacetylation was simply achieved under Zémplen conditions, furnishing **3** nearly quantitatively. Subsequent transformation of the double bond in the terminal alcohol was realized by hydroboration–oxidation of the olefins **4** and **5** to produce the alcohols **6** and **7** in 72 and 82% yield, respectively. As side-products, the corresponding *sec* alcohols were observed (<10%), which were easily removed by column chromatography. X-ray diffraction studies of compound **7** (Figure 1) established its structure and confirmed the presence of the tetrahydrofuran ring as well as the β-linkage to the hydroxy alkyl residue, with C-1′ possessing *S*-configuration.



Scheme 1 Consecutive synthesis of alcohols **6**, **7**, and aldehydes **8** and **9** starting from the β-allyl *C*-glycoside of D-ribofuranose **2**. *Reagents and conditions*: (i) AllTMS, $ZnBr_2$, $MeNO_2$; (ii) cat. NaOMe in MeOH, 75 min, 20 °C; (iii) TBDMSCl or TBDPSCl, py, 12 h; (iv) B_2H_6–THF, 3 h, 0 °C, followed by H_2O_2, NaOH; (v) Swern oxidation.

Next, Swern oxidation[6] of the primary alcohols **6** and **7** gave the best results compared to other selective oxidation procedures, and aldehydes **8** and **9** were each obtained in 83% yield (Scheme 1).

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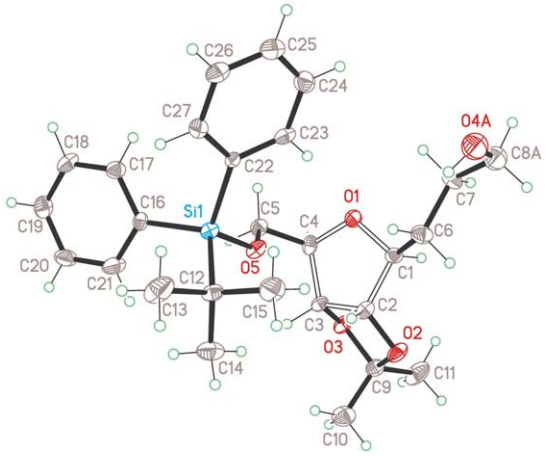


Figure 1 Molecular structure of alcohol **7** with atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Puckering parameters are q2 = 0.2602(2) and Φ2 = –62.77(4) for the tetrahydrofuran ring. Only one orientation of the disordered atoms C8 and O4 are shown.

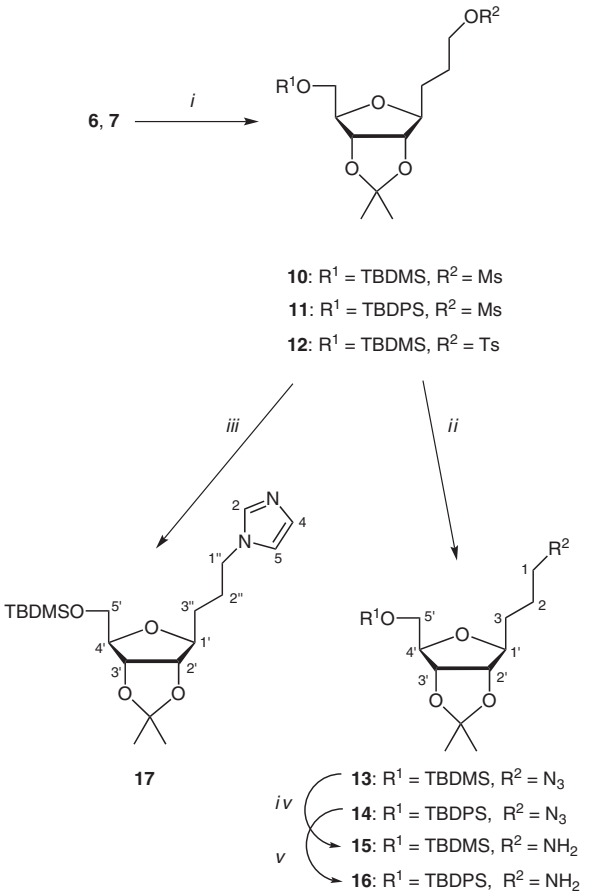
On the other hand, introduction of N-functionality was achieved via the sulfonates **10**–**12**, which are easily accessible in good to quantitative yield (Scheme 2). Mesylates **10** and **11** were treated with sodium azide in the presence of crown ether (18-crown-6) in anhydrous *N*,*N*′-dimethylformamide (DMF) to provide azides **13** and **14** in 85 and 89% yield, respectively. Catalytic hydrogenation of **13** afforded amine **15** in 65% yield. Comparable results were obtained by using a Staudinger reaction[7] to furnish amine **16** in 64% yield.

Optimal conditions for the alkylation of imidazole were found by using its sodium salt and mesylate **10** as coupling agent. Both reactions — mesylation of **6** as well as formation of **17** — were achieved in nearly quantitative yields.

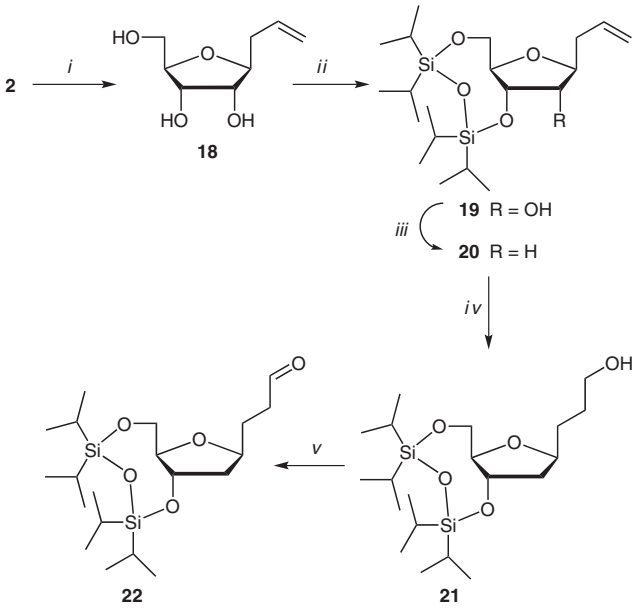
To prepare comparable key intermediates based on 2-deoxyribofuranose, a slightly modified synthetic route to **20** was applied starting from C-glycoside **2**. The total yield over four steps, including cleavage of the protecting groups of **2**, introduction of the 1,1,3,3-tetraisopropyldisiloxane group (TIPDS, **19**), exchange of the hydroxy group by iodine, and its reduction (**20**), was improved from 36 to 67% (Scheme 3). Gratifyingly, compound **19** provided suitable crystals, so that a single crystal X-ray analysis (Figure 2) confirmed our previous results.[5]

Employing the same conditions for the hydroboration–oxidation used for the preparation of **6** or **7** on olefin **20** provided the primary alcohol **21** in 69% yield. Consecutive Swern oxidation was also attempted to furnish aldehyde **22**. However, this proved unsuccessful, with many side-products being observed. Alternatively, the Dess–Martin variant[8,9] gave aldehyde **22** in 79% yield (Scheme 3).

To allow further variation in heterocyclic chemistry, which will be described in future publications, the chemistry was expanded to include acetylenic ketones.[10,11]



Scheme 2 Synthesis of sulfonates **10**–**12** and their transformation into nitrogen derivatives **13**–**17**. *Reagents and conditions*: (i) MsCl, Et_3N, CH_2Cl_2, 20 min, 5 °C, and PTSCl, py,12 h, 5–20 °C; (ii) NaN_3, 18-crown-6, DMF, 24 h, 20 °C; (iii) Na imidazolide, DMF, 3 h, 60 °C; (iv) Pd/C, MeOH, H_2 atmosphere, 8 h, 20 °C; (v) Ph_3P, THF, 90 min, 20 °C, then H_2O, 24 h, 20 °C.



Scheme 3 Consecutive synthesis of alcohol **21** and aldehyde **22** starting from the β-allyl *C*-glycoside of 2-deoxy-D-ribofuranose **20**. *Reagents and conditions*: (i) aq HCl, EtOH, 2 d, 20 °C; (ii) TIPDSCl, imidazole, DMF, 1 h, 5 °C; (iii) I_2, Ph_3P, imidazole, toluene, then Bu_3SnH, AIBN, toluene,10 h, reflux; (iv) B_2H_6–THF, 3 h, 0 °C, followed by H_2O_2, NaOH; (v) Dess–Martin oxidation.

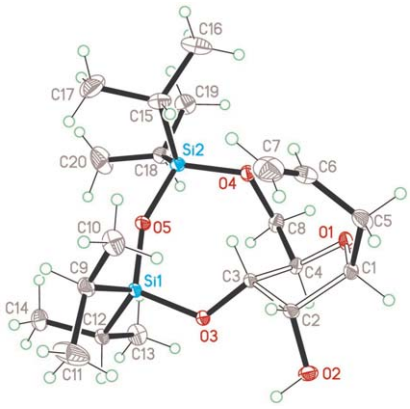
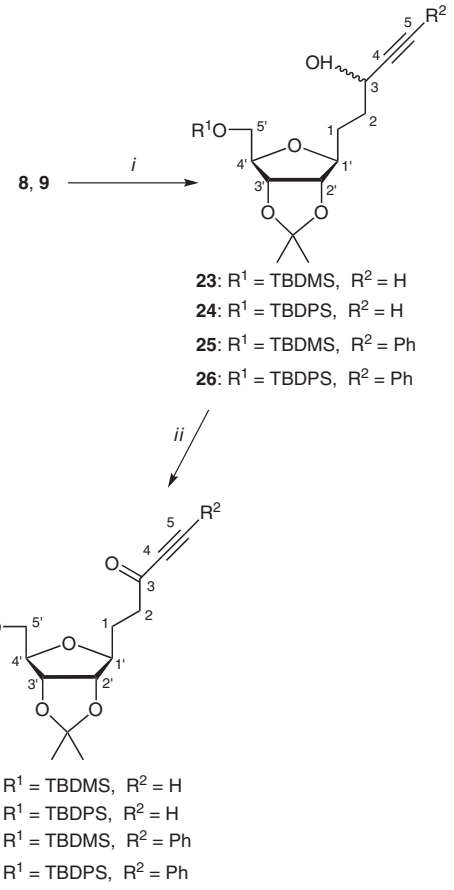
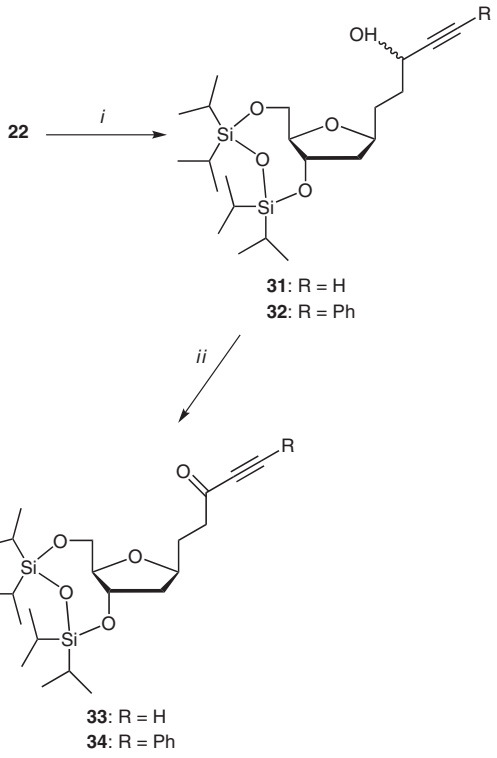


Figure 2 Molecular structure of *C*-allyl derivative **19** with atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Puckering parameters are q2 = 0.420(1) and Φ2 = –62.7(2) for the tetrahydrofuran ring.

Treatment of aldehydes **8** or **9** with ethynylmagnesium bromide or phenylethynyllithium in anhydrous tetrahydrofuran (THF) afforded pentynols **23**–**26** as an inseparable diastereomeric mixture in 64, 83, 67, and 69% yield, respectively (Scheme 4). The stereogenic center giving rise to diastereoisomers will be destroyed in the subsequent step. Thus, oxidation of **23** and **25** was accomplished by using Dess–Martin reagent, whereas oxidation of **24** and **26** was achieved by treatment with pyridinium chlorochromate (PCC) to provide the ethynyl ketones **27** and **29** in 82 and 90% yield, respectively, and ketones **28** and **30** were obtained in 54 and 50% yield, respectively. Following the above strategy, alcohols **31** and **32** were obtained in 75 and 66% isolated yield, respectively. The corresponding alkynyl ketones **33** and **34** were synthesized by Dess–Martin oxidation and isolated in 77 and 60% yield, respectively (Scheme 5).



Scheme 4 Synthesis of acetylenic ketones **27**–**30** derived from D-ribofuranose C-glycoside. *Reagents and conditions*: (i) ethynylmagnesium bromide or phenylethynyllithium, THF, 4 h, 20 °C; (ii) Dess–Martin oxidation gave **27** and **29**, PCC oxidation provided **28** and **30.**



Scheme 5 Synthesis of acetylenic ketones **33** and **34** derived from 2-deoxy-D-ribofuranose C-glycoside. *Reagents and conditions*: (i) ethynylmagnesium bromide or phenylethynyllithium, THF, 4 h, 20 °C; (ii) Dess–Martin oxidation.

In conclusion, we have developed a versatile synthetic approach to key intermediates of nucleoside analogues. The route allows the synthesis of a broad variety of heterocyclic β-C-glycosidic moieties connected to D-ribofuranose and 2-deoxy-D-ribofuranose. Examples of such structures will be reported in due course.

Melting points were determined with a Boetius micro-heating plate BHMK 05 (Rapido, Dresden) and are not corrected. Optical rotation was measured for solutions in a 2-cm cell with an automatic polarimeter GYROMAT (Dr. Kernchen Co.). ^{1}H NMR (250.13 MHz and 300.13 MHz) and ^{13}C NMR (62.9 MHz and 75.5 MHz) spectra were recorded with Bruker AV 250 and AV 300 instruments, respectively, with $CDCl_3$ as solvent. Calibration of the spectra was carried out with solvent signals ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm). ^{1}H and ^{13}C NMR signals were assigned by DEPT, two-dimensional ^{1}H,^{1}H COSY and ^{1}H,^{13}C correlation spectra (HMBC and HSQC). For NMR numbering of atoms see Scheme 1, Scheme 2, and Scheme 4. Mass spectra were recorded with an AMD 402/3 spectrometer (AMD Intectra GmbH). Elemental anal-

ysis was performed with a CHNS-Flash-EA-1112 instrument (Thermoquest).

For X-ray structure determination of compounds **7** and **19**, an X8Apex system with CCD area detector was used (λ = 0.71073 Å; graphite monochromator). The structures were solved by direct methods (Bruker-SHELXTL). The refinement calculations were performed by the full-matrix least-squares method of Bruker SHELXTL (Version 5.10, Bruker Analytical X-ray Systems). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions and refined using riding models. Crystallographic data for the structure analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No 827041 and 825615 for compounds **7** and **19**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK; Fax +44(1223)336033 or via Email: deposit@ccdc.cam.ac.uk or online at http://www.ccdc.cam.ac.uk.

All washing solutions were cooled to ~5 °C. The $NaHCO_3$ solution was saturated. Reactions were monitored by thin-layer chromatography (TLC; Silica Gel 60, F_{254}, Merck KGaA). The following solvent systems (v/v) were used: (A_1) 1.5:1, (A_2) 2:1, (A_3) 2.5:1, (A_4) 3:1, (A_5) 4:1, (A_6) 5:1, (A_7) 6:1, (A_8) 7:1, (A_9) 8:1, (A_{10}) 10:1, (A_{11}) 11:1, (A_{12}) 12:1, (A_{13}) 80:1 *n*-hexane–EtOAc; (B_1) 1:1, (B_2) 2:1, (B_3) 15:1 EtOAc–MeOH. TLC spots were made visible by dipping the TLC plates into a methanolic 10% H_2SO_4 solution and charring with a heat gun for 3–5 min. Preparative flash chromatography was performed by elution from columns of slurry-packed Silica Gel 60 (Merck, 63–200 μm). All solvents and reagents were purified and dried according to standard procedures.[12] After classical workup of the reactions mixtures, the organic layer was dried over $MgSO_4$, and then concentrated under reduced pressure (rotary evaporator).

3-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranosyl)prop-1-ene (4)

NaOMe (0.5 M in MeOH, 0.8 mL) was added to a soln of **2** (7.30 g, 28.5 mmol) in anhyd MeOH (40 mL). After stirring at ambient temperature for 75 min (TLC; solvent A_2), the reaction mixture was neutralized with IR120 (H^+) Amberlite resin, filtered, dried, and concentrated. Compound **3** was obtained quantitatively and used in the next step without further purification.

A soln of *tert*-butylchlorodimethylsilane (5.43 g, 36.0 mmol) in anhyd pyridine (12 mL) was added dropwise to a stirred soln of **3** (6.10 g, 28.5 mmol) in anhyd pyridine (60 mL) at 0 °C. The mixture was allowed to come to r.t. and stirring was continued overnight (reaction monitored by TLC). The reaction mixture was diluted with EtOH–heptane–$CHCl_3$ (1:1:5, v/v/v; 100 mL) and concentrated. After dissolving the residue in heptane–$CHCl_3$ (2:1, v/v; 360 mL), the organic phase was washed successively with aq 15% $NaHSO_4$ (2 × 120 mL), ice–water (120 mL), and $NaHCO_3$ (2 × 120 mL), dried, and concentrated. Purification by flash chromatography (solvent A_{10}) afforded compound **4**.

Yield: 8.80 g (94%); colorless syrup; $[\alpha]_D^{23}$ –12.1 (*c* 1.1, $CHCl_3$); R_f = 0.38 (solvent A_{10}).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.06, 0.07 [2 × s, 6 H, $Si(CH_3)_2$], 0.90 [s, 9 H, $C(CH_3)_3$], 1.34, 1.52 [2 × s, 6 H, $C(CH_3)_2$], 2.37 (m, 2 H, H-3), 3.72 (m, 2 H, H-5′), 3.95 (app dt, $^3J_{1',3a}$ = 6.5 Hz, $^3J_{1',2'} \approx {}^3J_{1',3b}$ = 4.7 Hz, 1 H, H-1′), 4.00 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.6 Hz, 1 H, H-4′), 4.33 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{1',2'}$ = 4.7 Hz, 1 H, H-2′), 4.62 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{3',4'}$ = 3.6 Hz, 1 H, H-3′), 5.05–5.19 (m, 2 H, H-1), 5.84 (m, 1 H, H-2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.4, –5.3 [$Si(CH_3)_2$], 18.4 [$C(CH_3)_3$], 25.6, 27.5 [$C(CH_3)_2$], 25.9 [$C(CH_3)_3$], 38.1 (C-3), 63.6 (C-5′), 81.8 (C-3′), 83.9, 84.3, 84.4 (C-1′,2′,4′), 117.4 (C-1), 134.0 (C-2), 113.8 [$C(CH_3)_2$].

Anal. Calcd for $C_{17}H_{32}O_4Si$ (328.52): C, 62.15; H, 9.82. Found: C, 61.99; H, 9.73.

Compound **5** was previously obtained by the reaction of allyltrimethylsilane with 1-*O*-acetyl-5-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-β-D-ribofuranose.[5] In principle, the procedure above can be used analogously for its preparation by using *tert*-butylchlorodiphenylsilane.

Hydroboration–Oxidation of Compounds 4 and 5

Borane–tetrahydrofuran complex (0.1 M in THF, 50.0 mL) was added dropwise to a stirred soln of **4** (5.91 g, 18.0 mmol) or **5** (8.15 g, 18.0 mmol) in anhyd THF (50 mL) at 0 °C, and stirring was continued at that temperature. After 3 h, the excess of borane complex was destroyed by adding a few drops of H_2O. NaOH (3 M, 215 mL) and 30% H_2O_2 (215 mL) were then added successively to the reaction mixture at 0 °C. The ice-bath was removed and the mixture was stirred for 90 min at ambient temperature (reaction monitored by TLC). The reaction mixture was poured into ice–water (600 mL), the aqueous phase was extracted with CH_2Cl_2 (4 × 300 mL), and the combined organic phases were washed with brine (250 mL), dried, and concentrated. Purification by flash chromatography (solvent A_2) afforded **6** and **7**.

3-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)propan-1-ol (6)

Purified by flash chromatography (solvent A_2).

Yield: 3.92 g (66%); colorless syrup; $[\alpha]_D^{24}$ –7.4 (*c* 1.2, $CHCl_3$); R_f = 0.2 (solvent A_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.05, 0.05 [2 × s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $C(CH_3)_3$], 1.32, 1.51 [2 × s, 6 H, $C(CH_3)_2$], 1.55–1.81 (m, 4 H, H-2,3), 2.25 (br s, 1 H, OH), 3.63 (m, 2 H, H-1), 3.70 (m, 2 H, H-5′), 3.83–3.90 (m, 1 H, H-1′), 4.00 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.6 Hz, 1 H, H-4′), 4.26 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.0 Hz, 1 H, H-2′), 4.61 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.6 Hz, 1 H, H-3′).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.5, –5.4 [$Si(CH_3)_2$], 18.3 [$C(CH_3)_3$], 25.5, 27.4 [$C(CH_3)_2$], 25.8 [$C(CH_3)_3$], 29.3, 30.5 (C-2,3), 62.5, 63.5 (C-1,5′), 81.7 (C-3′), 84.4, 84.6, 84.9 (C-1′,2′,4′), 114.0 [$C(CH_3)_2$].

Anal. Calcd for $C_{17}H_{34}O_5Si$ (346.53): C, 58.92; H, 9.89. Found: C, 58.80; H, 9.94.

3-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)propan-1-ol (7)

Purified by flash chromatography (solvent A_2).

Yield: 6.95 g (82%); colorless crystals; mp 50–52 °C (EtOAc–hexane); $[\alpha]_D^{23}$ –2.6 (*c* 1.0, $CHCl_3$); R_f = 0.28 (solvent A_2).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.06 [s, 9 H, $C(CH_3)_3$], 1.35, 1.53 [2 × s, 6 H, $C(CH_3)_2$], 1.60–1.80 (m, 4 H, H-2,3), 3.66 (m, 2 H, H-5′), 3.75 (m, 2 H, H-1), 3.84–3.92 (m, 1 H, H-1′), 4.06 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.6 Hz, 1 H, H-4′), 4.31 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.0 Hz, 1 H, H-2′), 4.71 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.6 Hz, 1 H, H-3′), 7.34–7.72 (m, 10 H, PhH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.2 [$C(CH_3)_3$], 25.6, 27.0 [$C(CH_3)_2$], 26.5 [$C(CH_3)_3$], 29.5, 30.6 (C-2,3), 62.7 (C-1), 64.1 (C-5′), 81.8 (C-3′), 84.2, 84.5, 84.8 (C-1′,2′,4′), 114.2 [$C(CH_3)_2$], 127.7 (2), 135.6, 135.7 (*o*-, *m*-Ph), 129.7 (2) (*p*-Ph), 133.2, 133.3 (*i*-Ph).

MS (EI): *m*/*z* (%) = 471 (3) $[M + H]^+$.

Anal. Calcd for $C_{27}H_{38}O_5Si$ (470.67): C, 68.90; H, 8.14. Found: C, 68.64; H, 8.15.

Swern Oxidation of 6 and 7

DMSO (2.1 mL, 30.0 mmol) was added dropwise to a stirred soln of oxalyl chloride (1.7 mL, 20.0 mmol) in anhyd CH_2Cl_2 (4.0 mL)

at –72 °C under an Ar atmosphere. After stirring the mixture for 10 min, a soln of **6** (4.85 g, 14.0 mmol) or **7** (6.59 g, 14.0 mmol) in anhyd CH_2Cl_2 (9.0 mL) was added dropwise at –72 °C. Stirring was continued for a further 15 min before Et_3N (8.9 mL, 64 mmol) was added dropwise. To facilitate stirring, an additional amount of CH_2Cl_2 (10 mL) was added and the mixture was warmed to r.t. After stirring for 1 h at r.t., H_2O (30 mL) was added, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were then washed with $NaHCO_3$ (90 mL), dried, and concentrated. The residue was purified by flash chromatography to afford compound **8** (86%) as a colorless syrup or compound **9** (83%) as a colorless solid.

3-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranosyl-1-yl)propanal (8)
Purified by flash chromatography (solvent A_5).

Yield: 4.15 g (86%); colorless syrup; $[\alpha]_D^{22}$ –14.4 (*c* 1.0, $CHCl_3$); R_f = 0.31 (solvent A_5).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.05, 0.05 [2 × s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.33, 1.51 [2 × s, 6 H, $C(CH_3)_2$], 1.80–2.03 (m, 2 H, H-3), 2.47–2.66 (m, 2 H, H-2), 3.69 (m, 2 H, H-5′), 3.86 (app dt, $^3J_{1',3a}$ = 8.0 Hz, $^3J_{1',2'} \approx {}^3J_{1',3b}$ = 5.0 Hz, 1 H, H-1′), 3.99 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.5 Hz, 1 H, H-4′), 4.27 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{1',2'}$ = 5.0 Hz, 1 H, H-2′), 4.62 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{3',4'}$ = 3.5 Hz, 1 H, H-3′), 9.77 (t, $^3J_{1,2}$ = 1.4 Hz, 1 H, H-1).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.5, –5.3 [$Si(CH_3)_2$], 18.3 [*C*$(CH_3)_3$], 25.5, 27.5 [C(*C*$H_3)_2$], 25.9 [C(*C*$H_3)_3$], 26.1 (C-3), 40.2 (C-2), 63.6 (C-5′), 81.9 (C-3′), 83.6, 84.5, 84.8 (C-1′,2′,4′), 114.0 [*C*$(CH_3)_2$], 201.6 (C-1).

Anal. Calcd for $C_{17}H_{32}O_5Si$ (344.52): C, 59.27; H, 9.36. Found: C, 57.71; H, 8.93.

3-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranosyl-1-yl)propanal (9)
Purified by flash chromatography (solvent A_5).

Yield: 5.45 g (83%); colorless solid; mp 54–56 °C; $[\alpha]_D^{21}$ –3.1 (*c* 1.0, $CHCl_3$); R_f = 0.20 (solvent A_2).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.06 [s, 9 H, $C(CH_3)_3$], 1.34, 1.53 [2 × s, 6 H, $C(CH_3)_2$], 1.77–2.07 (m, 2 H, H-3), 2.54–2.61 (m, 2 H, H-2), 3.77 (m, 2 H, H-5′), 3.86 (app dt, $^3J_{1',3a}$ = 8.2 Hz, $^3J_{1',2'} \approx {}^3J_{1',3b}$ = 5.2 Hz, 1 H, H-1′), 4.03 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.7 Hz, 1 H, H-4′), 4.30 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.2 Hz, 1 H, H-2′), 4.71 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.7 Hz, 1 H, H-3′), 7.34–7.44 (m, 6 H), 7.65–7.71 (m, 4 H, Ph), 9.76 (t, $^3J_{1,2}$ = 1.4 Hz, 1 H, H-1).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.3 [*C*$(CH_3)_3$], 25.6, 27.5 [C(*C*$H_3)_2$], 26.1 (C-3), 26.8 [C(*C*$H_3)_3$], 40.2 (C-2), 64.1 (C-5′), 81.9 (C-3′), 83.4, 84.2, 84.7 (C-1′,2′,4′), 114.3 [*C*$(CH_3)_2$], 127.2, 127.7, 135.6, 135.6 (*o*-, *m*-Ph), 129.7, 129.8 (*p*-Ph), 133.2, 133.3 (*i*-Ph), 201.6 (C-1).

MS (EI): *m*/*z* (%) = 469 (5) $[M + H]^+$.

Anal. Calcd for $C_{27}H_{36}O_5Si$ (468.66): C, 69.20; H, 7.74. Found: C, 69.45; H, 7.74.

Mesylation of Compounds 6 and 7
Methanesulfonyl chloride (5.9 mL, 42.0 mmol) was added dropwise to a stirred soln of **6** (2.77 g, 8.0 mmol) or **7** (3.77 g, 8.0 mmol) in anhyd CH_2Cl_2 (130 mL) and Et_3N (1.4 mL, 18.0 mmol) at 5 °C. After stirring for 20 min at r.t. (reaction monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (270 mL), and the organic phase was washed successively with $NaHCO_3$ (160 mL) and brine (160 mL), dried, and concentrated. Purification by flash chromatography afforded compound **10** (94%) and **11** (92%), both as colorless syrups.

3-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)prop-1-yl Methanesulfonate (10)
Purified by flash chromatography (solvent A_4).

Yield: 3.19 g (94%); colorless syrup; $[\alpha]_D^{23}$ –15.8 (*c* 1.1, $CHCl_3$); R_f = 0.17 (solvent A_4).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.05, 0.06 [2 × s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.33, 1.51 [2 × s, 6 H, $C(CH_3)_2$], 1.60–1.80 (m, 2 H, H-3), 1.82–1.96 (m, 2 H, H-2), 2.99 (s, 3 H, SO_2CH_3), 3.70 (m, 2 H, H-5′), 3.84 (app dt, $^3J_{1',3a}$ = 7.7 Hz, $^3J_{1',2'} \approx {}^3J_{1',3b}$ = 5.2 Hz, 1 H, H-1′), 4.00 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.6 Hz, 1 H, H-4′), 4.19–4.31 (m, 3 H, H-1,2′), 4.61 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.6 Hz, 1 H, H-3′).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.4, –5.3 [$Si(CH_3)_2$], 18.3 [*C*$(CH_3)_3$], 25.5, 27.4 [C(*C*$H_3)_2$], 25.6 (C-2), 25.9 [C(*C*$H_3)_3$], 29.5 (C-3), 37.3 (SO_2CH_3), 63.5 (C-5′), 69.6 (C-1), 81.8 (C-3′), 83.8, 84.4, 84.8 (C-1′,2′,4′), 114.0 [*C*$(CH_3)_2$].

Anal. Calcd for $C_{18}H_{36}O_7SSi$ (424.62): C, 50.91; H, 8.55; S, 7.55. Found: C, 51.17; H, 8.45; S, 7.50.

3-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)prop-1-yl Methanesulfonate (11)
Purified by flash chromatography (solvent A_1).

Yield: 4.04 g (92%); colorless syrup. Compound **11** was used in the next step without further analytical characterization.

3-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)prop-1-yl 4-Methylbenzenesulfonate (12)
A soln of 4-methylbenzenesulfonyl chloride (763 mg, 4.0 mmol) in anhyd pyridine (3 mL) was added dropwise to a stirred soln of **6** (692 mg, 2.0 mmol) in anhyd pyridine (11 mL) at 5 °C. The ice bath was removed and the mixture was stirred for 12 h at r.t. After adding toluene–heptane (5:1, 60 mL), the reaction mixture was concentrated, the residue was dissolved in CH_2Cl_2 (100 mL), and the organic phase was successively washed with aq 15% $NaHSO_4$ (2 × 40 mL), ice-water (40 mL), $NaHCO_3$ (2 × 40 mL), dried, and concentrated. Purification by flash chromatography (solvent A_6) afforded compound **12**.

Yield: 651 mg (65%); colorless syrup; $[\alpha]_D^{23}$ –15.5 (*c* 1.0, $CHCl_3$); R_f = 0.17 (solvent A_6).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.03, 0.04 [2 × s, 6 H, $Si(CH_3)_2$], 0.87 [s, 9 H, $C(CH_3)_3$], 1.31, 1.49 [2 × s, 6 H, $C(CH_3)_2$], 1.54–1.67 (m, 2 H, H-3), 1.70–1.84 (m, 2 H, H-2), 2.44 (s, 3 H, PhCH_3), 3.67 (m, 2 H, H-5′), 3.75 (app dt, $^3J_{1',3a}$ = 7.4 Hz, $^3J_{1',2'} \approx {}^3J_{1',3b}$ = 5.2 Hz, 1 H, H-1′), 3.94 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.6 Hz, 1 H, H-4′), 4.05 (m, 2 H, H-1), 4.19 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{1',2'}$ = 5.2 Hz, 1 H, H-2′), 4.58 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{3',4'}$ = 3.6 Hz, 1 H, H-3′), 7.33 (m, 2 H), 7.78 (m, 2 H, Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.4, –5.3 [$Si(CH_3)_2$], 18.3 [*C*$(CH_3)_3$], 21.6 (Ph*C*H_3), 25.3 (C-2), 25.5, 27.4 [C(*C*$H_3)_2$], 25.9 [C(*C*$H_3)_3$], 29.5 (C-3), 63.6 (C-5′), 70.2 (C-1), 81.8 (C-3′), 83.7, 84.4, 84.8 (C-1′,2′,4′), 114.0 [*C*$(CH_3)_2$], 127.9, 129.8 (*o*-, *m*-Ph), 133.2 (*i*-Ph), 144.6 (*p*-Ph).

Anal. Calcd for $C_{24}H_{40}O_7SSi$ (500.72): C, 57.57; H, 8.05; S, 6.40. Found: C, 57.81; H, 7.86; S, 6.17.

Azides 13 and 14
Mesylate **10** (2.12 g, 5.0 mmol) or **11** (2.74 g, 5.0 mmol), NaN_3 (3.9 g, 60 mmol), and crown ether (18-crown-6; 1.6 g, 6.0 mmol) in anhyd DMF (25 mL) was stirred for 24 h at r.t. The reaction mixture was diluted with EtOAc (250 mL), and the organic phase was washed with H_2O (2 × 150 mL), dried, and concentrated. Purification by flash chromatography afforded azide **13** (85%) or azide **14** (89%) both as colorless syrups.

3-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)propyl-1-azide (13)

Purified by flash chromatography (solvent A_{12}).

Yield: 1.58 g (85%); colorless syrup; $[\alpha]_D^{24}$ –23.3 (*c* 1.0, $CHCl_3$); R_f = 0.31 (solvent A_{10}).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.06, 0.06 [2 × s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.34, 1.52 [2 × s, 6 H, $C(CH_3)_2$], 1.57–1.82 (m, 4 H, H-2,3), 3.31 (m, 2 H, H-1), 3.71 (m, 2 H, H-5′), 3.84 (m, 1 H, H-1′), 3.99 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.6 Hz, 1 H, H-4′), 4.26 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.0 Hz, 1 H, H-2′), 4.62 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.6 Hz, 1 H, H-3′).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.4, –5.3 [$Si(CH_3)_2$], 18.3 [$C(CH_3)_3$], 25.3, 30.8 (C-2,3), 25.5, 27.5 [$C(CH_3)_2$], 25.9 [$C(CH_3)_3$], 51.3 (C-1), 63.6 (C-5′), 81.9 (C-3′), 84.0, 84.4, 84.9 (C-1′,2′,4′), 114.0 [$C(CH_3)_2$].

Anal. Calcd for $C_{17}H_{33}N_3O_4Si$ (371.55): C, 54.95; H, 8.95; N, 11.31. Found: C, 55.20; H, 9.00; N, 11.58.

3-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)propyl-1-azide (14)

Purified by flash chromatography (solvent A_{10}).

Yield: 2.21 g (89%); colorless syrup; $[\alpha]_D^{24}$ +0.6 (*c* 0.7, CH_2Cl_2); R_f = 0.44 (solvent A_6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.06 [s, 9 H, $C(CH_3)_3$], 1.35, 1.54 [2 × s, 6 H, $C(CH_3)_2$], 1.64–1.80 (m, 4 H, H-2,3), 3.30 (m, 2 H, H-1), 3.78 (m, 2 H, H-5′), 3.85 (m, 1 H, H-1′), 4.03 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.7 Hz, 1 H, H-4′), 4.29 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.2 Hz, 1 H, H-2′), 4.72 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.7 Hz, 1 H, H-3′), 7.35–7.44 (m, 6 H), 7.66–7.72 (m, 4 H, Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.3 [$C(CH_3)_3$], 25.4, 30.8 (C-2,3), 25.7, 27.5 [$C(CH_3)_2$], 26.8 [$C(CH_3)_3$], 51.3 (C-1), 64.1 (C-5′), 81.8 (C-3′), 83.9, 84.2, 84.9 (C-1′,2′,4′), 114.2 [$C(CH_3)_2$], 127.6, 127.7, 135.6, 135.6 (*o*-, *m*-Ph), 129.7, 129.8 (*p*-Ph), 133.2, 133.3 (*i*-Ph).

MS (CI): *m*/*z* (%) = 496 (40) $[M + H]^+$.

Anal. Calcd for $C_{27}H_{37}N_3O_4Si$ (495.69): C, 65.42; H, 7.52; N, 8.48. Found: C, 65.21; H, 7.76; N, 8.54.

3-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)propan-1-amine (15)

10% Pd/C (ca. 170 mg) was added to a soln of azide **13** (743 mg, 2.0 mmol) in MeOH (55 mL). The suspension was stirred for 8 h at r.t. under an atmosphere of H_2 (reaction monitored by TLC). The mixture was then filtered through Celite, eluted with MeOH, and the combined filtrates were concentrated. The crude product was purified by flash chromatography (solvent B_2) to give compound **15**.

Yield: 449 mg (65%); colorless syrup; $[\alpha]_D^{25}$ –12.5 (*c* 1.0, MeOH); R_f = 0.1 (solvent B_2).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.05, 0.05 [2 × s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $C(CH_3)_3$], 1.32, 1.51 [2 × s, 6 H, $C(CH_3)_2$], 1.54–1.65 (m, 4 H, H-2,3), 1.80 (br s, 2 H, NH_2), 2.72 (m, 2 H, H-1), 3.70 (m, 2 H, H-5′), 3.84 (m, 1 H, H-1′), 3.97 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.7 Hz, 1 H, H-4′), 4.25 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 4.9 Hz, 1 H, H-2′), 4.60 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.7 Hz, 1 H, H-3′).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.4, –5.3 [$Si(CH_3)_2$], 18.3 [$C(CH_3)_3$], 25.5, 27.5 [$C(CH_3)_2$], 25.9 [$C(CH_3)_3$], 29.7, 31.1 (C-2,3), 41.9 (C-1), 63.6 (C-5′), 81.9 (C-3′), 84.3, 84.4 (C-1′,4′), 85.0 (C-2′), 113.9 [$C(CH_3)_2$].

Anal. Calcd for $C_{17}H_{35}NO_4Si$ (345.55): C, 59.09; H, 10.21; N, 4.05. Found: C, 59.30; H, 9.92; N, 3.87.

3-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)propan-1-amine (16)

A soln of azide **14** (991 mg, 2.0 mmol) and Ph_3P (551 mg, 2.1 mmol) in THF (20 mL) was stirred for 90 min at r.t. (reaction monitored by TLC). After adding H_2O (8 mL, 0.44 mmol), the reaction mixture was stirred for 24 h at r.t. and then concentrated. The residue was purified by flash chromatography (solvent B_2) to provide compound **16**.

Yield: 600 mg (64%); colorless syrup; $[\alpha]_D^{24}$ –3.0 (*c* 1.0, MeOH); R_f = 0.16 (solvent B_1).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.05 [s, 9 H, $C(CH_3)_3$], 1.34, 1.53 [2 × s, 6 H, $C(CH_3)_2$], 1.56–1.67 (m, 4 H, H-2,3), 1.90 (br s, 2 H, NH_2), 2.73 (m, 2 H, H-1), 3.77 (m, 2 H, H-5′), 3.86 (m, 1 H, H-1′), 4.02 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.8 Hz, 1 H, H-4′), 4.30 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.1 Hz, 1 H, H-2′), 4.70 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.8 Hz, 1 H, H-3′), 7.34–7.45 (m, 6 H), 7.66–7.72 (m, 4 H, Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.3 [$C(CH_3)_3$], 25.6, 27.5 [$C(CH_3)_2$], 26.8 [$C(CH_3)_3$], 29.5 (C-2), 31.1 (C-3), 41.9 (C-1), 64.2 (C-5′), 81.9 (C-3′), 84.1 (C-4′), 84.3 (C-1′), 85.0 (C-2′), 114.1 [$C(CH_3)_2$], 127.6, 127.7, 135.6, 135.7 (*o*-, *m*-Ph), 129.7, 129.7 (*p*-Ph), 133.3, 133.4 (*i*-Ph).

MS (CI): *m*/*z* (%) = 470 (100) $[M + H]^+$.

Anal. Calcd for $C_{27}H_{39}NO_4Si$ (469.69): C, 69.04; H, 8.37; N, 2.98. Found: C, 68.76; H, 8.30; N, 2.88.

1-[3-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)propyl]-1*H*-imidazole (17)

Methanesulfonate **10** (3.40 g, 8.0 mmol) was added to a soln of sodium imidazolide (1.01 g, 11.2 mmol) in anhyd DMF (55 mL). After stirring at 60 °C for 3 h (reaction monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (270 mL) and stored in a refrigerator overnight. The reaction mixture was filtered and the filtrate was washed with brine (200 mL), dried, and concentrated. The residue was purified by flash chromatography (solvent B_3) to provide compound **17**. Using tosylate **12** under the same conditions gave compound **17** in 75% yield.

Yield: 2.95 g (93%); pale-yellow syrup; $[\alpha]_D^{24}$ –16.7 (*c* 1.0, MeOH); R_f = 0.33 (solvent B_3).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.03, 0.04 [2 × s, 6 H, $Si(CH_3)_2$], 0.87 [s, 9 H, $C(CH_3)_3$], 1.30, 1.50 [2 × s, 6 H, $C(CH_3)_2$], 1.56, 1.89 (2 × m, 4 H, H-2″,3″), 3.68 (m, 2 H, H-5′), 3.78 (m, 1 H, H-1′), 3.90–4.00 (m, 3 H, H-4′,1″), 4.19 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.2 Hz, 1 H, H-2′), 4.57 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.6 Hz, 1 H, H-3′), 6.89 (br s, 1 H), 7.03 (br s, 1 H), 7.44 (br s, 1 H) (H-2,4,5).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.5, –5.3 [$Si(CH_3)_2$], 18.3 [$C(CH_3)_3$], 25.4, 27.4 [$C(CH_3)_2$], 25.8 [$C(CH_3)_3$], 27.5, 30.4 (C-2″,3″), 46.7 (C-1″), 63.5 (C-5′), 81.7 (C-3′), 83.9, 84.3, 84.8 (C-1′,2′,4′), 114.1 [$C(CH_3)_2$], 118.7 (br), 129.4 (br), 137.0 (br, C-2,4,5).

Anal. Calcd for $C_{20}H_{36}N_2O_4Si$ (396.60): C, 60.57; H, 9.15; N, 7.06. Found: C, 60.36; H, 9.16; N, 7.05.

3-(β-D-Ribofuranosyl)prop-1-ene (18)

Starting from **2** (4.10 g, 16.0 mmol), compound **18** (2.59 g, 93%) was obtained according to the procedure of Otero Martinez et al. as a colorless solid.[5]

3-[3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-β-D-ribofuranosyl]prop-1-ene (19)

1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (5.3 mL, 17.0 mmol) was added to a soln of **2** (2.79 g, 16.0 mmol) and imidazole (4.63 g, 68.0 mmol) in anhyd DMF (40 mL). After stirring at 5 °C for 1 h (reaction monitored by TLC), the reaction mixture was poured into

ice-water (500 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 150 mL), and the combined organic phases were washed with $NaHCO_3$ (150 mL), dried, and concentrated. Purification by flash chromatography (solvent A_{11}) afforded compound **19**.

Yield: 7.08 g (68%); colorless solid; mp 28 °C; R_f = 0.30 (solvent A_{11}). NMR data and elemental analysis were in agreement with reported data.[5]

3-[2-Deoxy-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-β-D-*erythro*-pentofuranosyl]prop-1-ene (20)

Exchange of the hydroxy group of **19** by iodine to furnish 3-[2-deoxy-2-iodo-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-β-D-arabinofuranosyl]prop-1-ene (95%) was carried out as described by Otero Martinez et al., and the analytical data were in agreement with the published data.[5]

A mixture of the 2-iodo-compound (6.32 g, 12.0 mmol), tri-*n*-butyltin hydride (6.98 g, 24.0 mmol), and azobisisobutyronitrile (AIBN; 493 mg, 3.0 mmol) in toluene (150 mL) was stirred at reflux for 5 h, after which time, additional tri-*n*-butyltin hydride (3.48 g, 12.0 mmol) and AIBN (493 mg, 3.0 mmol) were added. Stirring under reflux was continued for a further 5 h, and the reaction mixture was then filtered and concentrated. The residue was dissolved in Et_2O (200 mL) and the organic phase was washed with 10% KF (50 mL), dried, and concentrated. Purification by flash chromatography (solvent A_{13}) afforded compound **20** (4.42 g, 92%) as a colorless syrup. All analytical data were identical to those reported previously.[5]

3-[3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-1,2-dideoxy-β-D-ribofuranos-1-yl]propan-1-ol (21)

Prepared as described for the preparation of **6**. Compound **20** (4.00 g, 10.0 mmol) gave alcohol **21** after purification by flash chromatography (solvent A_3).

Yield: 3.01 g (72%); colorless syrup; $[\alpha]_D^{22}$ –23.0 (*c* 1.0, CH_2Cl_2); R_f = 0.29 (solvent A_3).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.84–1.10 [m, 28 H, C*H*(C*H*$_3$)$_2$], 1.52–1.70 (m, 4 H, H-2,3), 1.79 (app dt, $^2J_{2'a,2'b}$ = 12.8 Hz, $^3J_{1',2'a} \approx {}^3J_{2'a,3'}$ = 8.0 Hz, 1 H, H-2′a), 2.04 (ddd, $^2J_{2'a,2'b}$ = 12.8 Hz, $^3J_{1',2'b}$ = 6.5 Hz, $^3J_{2'b,3'}$ = 4.2 Hz, 1 H, H-2′b), 2.10 (br, 1 H, OH), 3.57–3.78 (m, 4 H, H-1,4′,5′a), 3.96–4.13 (m, 2 H, H-1′,5′b), 4.37 (app dt, $^3J_{2'a,3'}$ = 8.0 Hz, $^3J_{3',4'}$ = 4.4 Hz, $^3J_{2'b,3'}$ = 4.2 Hz, 1 H, H-3′).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.5, 13.0, 13.4, 13.5 [*C*H(CH$_3$)$_2$], 16.9, 17.0, 17.1, 17.3, 17.4, 17.4 (2), 17.5 [CH(*C*H$_3$)$_2$], 29.4, 32.3 (C-2,3), 40.6 (C-2′), 62.8 (C-1), 63.9 (C-5′), 73.7 (C-3′), 77.8 (C-1′), 86.2 (C-4′).

MS (ESI): *m*/*z* (%) = 419 (100) $[M + H]^+$.

Anal. Calcd for $C_{20}H_{42}O_5Si_2$ (418.72): C, 57.37; H, 10.11. Found: C, 57.17; H, 9.97.

3-[3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-1,2-dideoxy-β-D-ribofuranos-1-yl]propanal (22)

A soln of 12-I-5-triacetoxyperiodinane (5.30 g, 12.5 mmol) in anhyd CH_2Cl_2 (25 mL) was added to a stirred soln of alcohol **21** (4.61 g 11.0 mmol) in anhyd CH_2Cl_2 (25 mL) at r.t. under an Ar atmosphere. After stirring for 5 h (reaction monitored by TLC), solid $NaHCO_3$ (2.1 g, 25.0 mmol) and silica gel were successively added and the suspension was concentrated. The residue was loaded onto a silica gel column, and purified by chromatography (solvent A_7) to provide the desired aldehyde **22**.

Yield: 3.63 g (79%); colorless syrup; $[\alpha]_D^{22}$ –24.1 (*c* 1.0, CH_2Cl_2); R_f = 0.42 (solvent A_6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.88–1.10 [m, 28 H, C*H*(C*H*$_3$)$_2$], 1.72–1.93 (m, 3 H, H-2′a,3), 1.99–2.10 (m, 1 H, H-2′b), 2.42–2.59 (m, 2 H, H-2), 3.72 (m, 2 H, H-4′,5′a), 3.95–4.13 (m, 2 H, H-1′,5′b), 4.36 (app dt, $^3J_{2'a,3'}$ = 7.9 Hz, $^3J_{3',4'}$ = 4.5 Hz, $^3J_{2'b,3'}$ = 4.2 Hz, 1 H, H-3′), 9.77 (t, $^3J_{1,2}$ = 1.5 Hz, 1 H, H-1).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.5, 12.9, 13.3, 13.5 [*C*H(CH$_3$)$_2$], 16.9, 17.0, 17.1, 17.3, 17.4, 17.4 (2), 17.6 [CH(*C*H$_3$)$_2$], 27.8, 30.3 (C-2,3), 40.3 (C-2′), 63.7 (C-5′), 73.5 (C-3′), 76.5 (C-1′), 86.0 (C-4′), 202.1 (C-1).

MS (ESI): *m*/*z* (%) = 417 (3) $[M + H]^+$.

Anal. Calcd for $C_{20}H_{40}O_5Si_2$ (416.70): C, 57.65; H, 9.68. Found: C, 57.70; H, 9.57.

Alkynylation of Aldehydes 8, 9, and 22

A soln of ethynylmagnesium bromide (0.5 M, 12 mL, 6.0 mmol) or lithium phenylacetylide (1.0 M, 10 mL, 10 mmol) in anhyd THF was added dropwise to a stirred soln of **8** (1.72 g, 5.0 mmol), **9** (2.34 g, 5.0 mmol), or **22** (2.09 g, 5.0 mmol) in anhyd THF (24 mL) at r.t. After stirring for 4 h (reaction monitored by TLC), H_2O (0.3 mL) and silica gel were successively added, and the suspension was concentrated. The residue was loaded onto a silica gel column and purified by flash chromatography to provide the desired ethynyl alcohols **23**–**26**, **31**, and **32** as diastereomeric mixtures.

(3*R*,*S*)-1-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)pent-4-yn-3-ol (23)

Purified by flash chromatography (solvent A_4).

Yield: 1.19 g (64%); colorless syrup; $[\alpha]_D^{23}$ –18.5 (*c* 1.0, $CHCl_3$); R_f = 0.3 (solvent A_4).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ (ratio ca. 1:1) = 0.06, 0.06 [2 × s, 6 H, Si(CH$_3$)$_2$], 0.89 [s, 9 H, C(CH$_3$)$_3$], 1.33, 1.52 [2 × s, 6 H, C(CH$_3$)$_2$], 1.79–1.91 (m, 4 H, H-1,2), 2.42 (d, $^4J_{3,5}$ = 2.1 Hz), 2.44 (d, $^4J_{3,5}$ = 2.1 Hz) (1 H, H-5), 2.59 (br s), 2.82 (br d, $^3J_{3,OH}$ = 5.9 Hz, 1 H, OH), 3.71 (m, 2 H, H-5′), 3.84–3.92 (m, 1 H, H-1′), 4.01 (m, 1 H, H-4′), 4.28 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{1',2'}$ = 5.2 Hz, 1 H, H-2′), 4.37–4.48 (m, 1 H, H-3), 4.62 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{3',4'}$ = 3.6 Hz), 4.63 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{3',4'}$ = 3.6 Hz) (1 H, H-3′).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.4 (2), –5.3 (2) [Si(CH$_3$)$_2$], 18.3 (2) [*C*(CH$_3$)$_3$], 25.5 (2), 27.5 (2) [C(*C*H$_3$)$_2$], 25.9 (2) [C(*C*H$_3$)$_3$], 28.9, 29.4 (C-1), 34.2 (C-2), 61.6, 62.0 (C-3), 63.5 (C-5′), 72.8, 72.9 (C-5), 81.8 (2) (C-3′), 84.2, 84.4, 84.5, 84.5, 84.7, 84.9 (C-1′,2′,4′), 84.7, 84.7 (C-4), 114.0 [*C*(CH$_3$)$_2$].

Anal. Calcd for $C_{19}H_{34}O_5Si$ (370.56): C, 61.58; H, 9.25. Found: C, 61.56; H, 9.23.

(3*R*,*S*)-1-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)pent-4-yn-3-ol (24)

Purified by flash chromatography (solvent A_5).

Yield: 2.05 g (83%); colorless syrup; $[\alpha]_D^{23}$ –1.1 (*c* 1.0, CH_2Cl_2); R_f = 0.45 (solvent A_2).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ (ratio ca. 1:1) = 1.06 [s, 9 H, C(CH$_3$)$_3$], 1.34, 1.53 [2 × s, 6 H, C(CH$_3$)$_2$], 1.81–1.94 (m, 4 H, H-1,2), 2.00 (br, 1 H, OH), 2.38 (d, $^4J_{3,5}$ = 2.1 Hz), 2.42 (d, $^4J_{3,5}$ = 2.1 Hz) (1 H, H-5), 3.78 (m, 2 H, H-5′), 3.83–3.94 (m, 1 H, H-1′), 4.02–4.08 (m, 1 H, H-4′), 4.32 (m, 1 H, H-2′), 4.37–4.48 (m, 1 H, H-3), 4.70 (m, 1 H, H-3′), 7.36–7.45 (m, 6 H), 7.65–7.72 (m, 4 H, Ph).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.2 (2) [*C*(CH$_3$)$_3$], 25.5 (2), 27.5 (2) [C(*C*H$_3$)$_2$], 26.8 (2) [C(*C*H$_3$)$_3$], 29.0, 29.4 (C-1), 34.2, 34.2 (C-2), 61.7, 62.0 (C-3), 64.0 (2) (C-5′), 72.9, 73.0 (C-5), 81.8 (2) (C-3′), 84.1, 84.2, 84.3, 84.4, 84.8, 84.8 (C-1′,2′,4′), 84.6, 84.6 (C-4), 114.2, 114.2 [*C*(CH$_3$)$_2$], 127.8 (4) (*m*-Ph), 129.7 (4) (*p*-Ph), 133.1, 133.2, 133.3, 133.3 (*i*-Ph), 135.6 (4) (*o*-Ph).

MS (CI): *m*/*z* (%) = 495 (3) $[M + H]^+$.

Anal. Calcd for $C_{29}H_{38}O_5Si$ (494.69): C, 70.41; H, 7.74. Found: C, 70.21; H, 7.86.

(3*R*,*S*)-1-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)-5-phenylpent-4-yn-3-ol (25)
Purified by flash chromatography (solvent A_5).

Yield: 1.50 g (67%); pale-yellow syrup; $[\alpha]_D^{23}$ –16.4 (*c* 1.0, CH_2Cl_2); R_f = 0.26 (solvent A_5).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ (ratio ca. 1:1) = 0.05, 0.06, 0.06, 0.06 [4 × s, 6 H, $Si(CH_3)_2$], 0.88, 0.89 [2 × s, 9 H, $C(CH_3)_3$], 1.34, 1.53 [2 × s, 6 H, $C(CH_3)_2$], 1.76–1.99 (m, 4 H, H-1,2), 2.57 (d, $^3J_{3,OH}$ = 5.3 Hz), 2.72 (d, $^3J_{3,OH}$ = 6.3 Hz) (1 H, OH), 3.72 (m, 2 H, H-5′), 3.88–3.96 (m, 1 H, H-1′), 4.02 (m, 1 H, H-4′), 4.31 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{1',2'}$ = 5.1 Hz, 1 H, H-2′), 4.60–4.71 (m, 2 H, H-3,3′), 7.27–7.32 (m, 3 H, *m*-, *p*-Ph), 7.40–7.43 (m, 2 H, *o*-Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.4, –5.4, –5.3, –5.3 [$Si(CH_3)_2$], 18.3, 18.3 [$C(CH_3)_3$], 25.5 (2), 27.5 (2) [$C(CH_3)_2$], 25.9 (2) [$C(CH_3)_3$], 29.2, 29.6 (C-1), 34.3, 34.4 (C-2), 62.4, 62.7 (C-3), 63.5 (2) (C-5′), 81.8, 81.8 (C-3′), 84.2, 84.4, 84.4, 84.5, 84.8, 84.9 (C-1′,2′,4′), 84.8, 84.8 (C-5), 89.9, 89.9 (C-4), 114.1 (2) [$C(CH_3)_2$], 122.7, 122.7 (*i*-Ph), 128.2 (2) (*m*-Ph), 128.3, 128.3 (*p*-Ph), 131.7 (2) (*o*-Ph).

Anal. Calcd for $C_{25}H_{38}O_5Si$ (446.65): C, 67.23; H, 8.58. Found: C, 67.11; H, 8.71.

(3*R*,*S*)-1-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)-5-phenylpent-4-yn-3-ol (26)
Purified by flash chromatography (solvent A_6).

Yield: 1.97 g (69%); pale-yellow syrup; $[\alpha]_D^{22}$ –0.9 (*c* 1.0, CH_2Cl_2); R_f = 0.45 (solvent A_2).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ (ratio ca. 1:1) = 1.04, 1.05 [2 × s, 9 H, $C(CH_3)_3$], 1.35, 1.54 [2 × s, 6 H, $C(CH_3)_2$], 1.80–2.05 (m, 4 H, H-1,2), 2.00 (br, 1 H, OH), 3.79 (m, 2 H, H-5′), 3.87–3.98 (m, 1 H, H-1′), 4.05 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.8 Hz, 1 H, H-4′), 4.33 (dd, $^3J_{2',3'}$ = 6.8 Hz, $^3J_{1',2'}$ = 5.2 Hz), 4.35 (dd, $^3J_{2',3'}$ = 6.8 Hz, $^3J_{1',2'}$ = 5.2 Hz) (1 H, H-2′), 4.60–4.75 (m, 2 H, H-3,3′), 7.25–7.32 (m, 3 H), 7.35–7.43 (m, 8 H), 7.65–7.73 (m, 4 H, Ph).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.2, 19.2 [$C(CH_3)_3$], 25.5 (2), 27.5 (2) [$C(CH_3)_2$], 26.8 (2) [$C(CH_3)_3$], 29.2, 29.6 (C-1), 34.4, 34.4 (C-2), 62.5, 62.7 (C-3), 64.1 (2) (C-5′), 81.8, 81.8 (C-3′), 84.1, 84.2, 84.2, 84.3, 84.8, 84.8 (C-1′,2′,4′), 84.9, 84.9 (C-5), 89.8, 89.9 (C-4), 114.2, 114.3 [$C(CH_3)_2$], 122.6, 122.7 (*i*-$Ph_{C\equiv C}$), 127.7 (4) (*m*-Ph), 128.2 (2) (*m*-$Ph_{C\equiv C}$), 128.3, 128.3 (*p*-$Ph_{C\equiv C}$), 129.7 (4) (*p*-Ph), 131.7 (2) (*o*-$Ph_{C\equiv C}$), 133.2 (2), 133.3 (2) (*i*-Ph), 135.6 (2), 135.7 (2) (*o*-Ph).

MS (CI): *m*/*z* (%) = 571 (7) $[M + H]^+$.

Anal. Calcd for $C_{35}H_{42}O_5Si$ (570.79): C, 73.65; H, 7.42. Found: C, 73.62; H, 7.43.

(3*R*,*S*)-1-[3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-1,2-dideoxy-β-D-ribofuranos-1-yl]pent-4-yn-3-ol (31)
Reaction time ca. 3 h; purified by flash chromatography (solvent A_6).

Yield: 1.71 g (75%); colorless syrup; $[\alpha]_D^{22}$ –22.1 (*c* 1.0, CH_2Cl_2); R_f = 0.29 (solvent A_6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = (ratio ca. 1:0.7) = 1.00–1.09 [m, 28 H, C*H*(CH_3)$_2$], 1.61–1.89 (m, 5 H, H-1,2,2′a), 2.00–2.10 (m, 1 H, H-2′b), 2.43 (d, $^4J_{3,5}$ = 2.2 Hz), 2.44 (d, $^4J_{3,5}$ = 2.2 Hz) (1 H, H-5), 2.57 (d, $^3J_{3,OH}$ = 5.2 Hz), 2.83 (d, $^3J_{3,OH}$ = 6.6 Hz) (1 H, OH), 3.67–3.79 (m, 2 H, H-4′,5′a), 3.97–4.16 (m, 2 H, H-1′,5′b), 4.35–4.50 (m, 2 H, H-3,3′).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.5 (2), 12.9 (2), 13.4 (2), 13.5 (2) [*C*H(CH_3)$_2$], 16.9 (2), 17.0 (2), 17.1 (2), 17.3 (2), 17.4 (4), 17.4 (2), 17.5 (2) [CH(*C*H_3)$_2$], 30.8, 31.1 (C-1), 34.2, 34.3 (C-2), 40.4, 40.6 (C-2′), 61.7, 62.1 (C-3), 63.8, 63.8 (C-5′), 72.7, 72.8 (C-5), 73.6, 73.7 (C-3′), 77.4, 77.7 (C-1′), 84.7, 84.8 (C-4), 86.2, 86.2 (C-4′).

MS (EI): *m*/*z* (%) = 456 (3) $[M]^+$.

Anal. Calcd for $C_{23}H_{44}O_5Si_2$ (456.76): C, 60.48; H, 9.71. Found: C, 60.72; H, 9.80.

(3*R*,*S*)-1-[3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-1,2-dideoxy-β-D-ribofuranos-1-yl]-5-phenylpent-4-yn-3-ol (32)
Reaction time ca. 3 h; purified by flash chromatography (solvent A_6).

Yield: 1.76 g (66%); pale-yellow syrup; $[\alpha]_D^{22}$ –12.3 (*c* 1.0, CH_2Cl_2); R_f = 0.30 (solvent A_6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ (ratio ca. 1:0.8) = 1.00–1.08 [m, 28 H, C*H*(CH_3)$_2$], 1.69–1.97 (m, 5 H, H-1,2,2′a), 2.01–2.12 (m, 1 H, H-2′b), 2.53 (d, $^3J_{3,OH}$ = 5.2 Hz), 2.77 (d, $^3J_{3,OH}$ = 6.5 Hz) (1 H, OH), 3.69–3.80 (m, 2 H, H-4′,5′a), 3.98–4.20 (m, 2 H, H-1′,5′b), 4.40, 4.65 (2 × m, 2 H, H-3,3′), 7.27–7.34 (m, 3 H, *m*-, *p*-Ph), 7.39–7.44 (m, 2 H, *o*-Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 12.5 (2), 12.9 (2), 13.4 (2), 13.5 (2) [*C*H(CH_3)$_2$], 16.9 (2), 17.0 (2), 17.1 (2), 17.3 (2), 17.4 (2), 17.4 (4), 17.5 (2) [CH(*C*H_3)$_2$], 31.0, 31.3 (C-1), 34.4, 34.5 (C-2), 40.5, 40.7 (C-2′), 62.5, 62.8 (C-3), 63.9 (2) (C-5′), 73.7, 73.7 (C-3′), 77.4, 77.7 (C-1′), 84.8, 84.9 (C-4), 86.2, 86.2 (C-4′), 89.9 (2) (C-5), 122.7, 122.7 (*i*-Ph), 128.2 (2) (*m*-Ph), 128.3, 128.3 (*p*-Ph), 131.7, 131.7 (*o*-Ph).

Anal. Calcd for $C_{29}H_{48}O_5Si_2$ (532.86): C, 65.37; H, 9.08. Found: C, 65.63; H, 8.88.

Oxidation of Alkynole 23–26, 31, and 32

Method A. Pyridinium Chlorochromate (PCC) Oxidation
PCC (800 mg, 3.7 mmol) was added to a soln of alkynol **24** (495 mg, 1.0 mmol) or **26** (571 mg, 1.0 mmol) in anhyd CH_2Cl_2 (40 mL). After stirring for 2 h (reaction monitored by TLC) at r.t., silica gel was added and the suspension was concentrated. The residue was loaded onto a silica gel column followed by flash chromatography to provide the desired ethynyl ketones **28** and **30** in 54 and 50% yield, respectively.

Method B. Dess–Martin Oxidation
A soln of alcohol **23** (3.71 g 10.0 mmol), **25** (4.47 g, 10.0 mmol), **31** (4.57 g, 10.0 mmol), or **32** (5.33 g, 10.0 mmol) in anhyd CH_2Cl_2 (20 mL) was added dropwise to a stirred soln of 12-I-5-triacetoxyperiodinane (10.60 g, 25.0 mmol), solid $NaHCO_3$ (1.6 g), and molecular sieves (4 Å, 15 g) in anhyd CH_2Cl_2 (400 mL) at 0 °C under an Ar atmosphere. After stirring for 4 h at r.t. (reaction monitored by TLC), solids were filtered off, and the filtrate was concentrated. The residue was purified by flash chromatography to provide the ethynyl ketones **27**, **29**, **33**, and **34** in 82, 90, 77, and 60%, respectively.

1-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)pent-4-yn-3-one (27)
Method B. Purified by flash chromatography (solvent A_8).

Yield: 3.02 g (82%); colorless syrup; $[\alpha]_D^{24}$ –28.4 (*c* 1.0, $CHCl_3$); R_f = 0.25 (solvent A_8).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.05, 0.06 [2 × s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.33, 1.51 [2 × s, 6 H, $C(CH_3)_2$], 1.83–2.05 (m, 2 H, H-1), 2.72 (m, 2 H, H-2), 3.21 (s, 1 H, H-5), 3.69 (m, 2 H, H-5′), 3.85 (app dt, $^3J_{1a,1'}$ = 8.0 Hz, $^3J_{1b,1'} \approx {}^3J_{1',2'}$ = 5.0 Hz, 1 H, H-1′), 4.00 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.5 Hz, 1 H, H-4′), 4.27 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{1',2'}$ = 5.0 Hz, 1 H, H-2′), 4.62 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{3',4'}$ = 3.5 Hz, 1 H, H-3′).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –5.5, –5.3 [$Si(CH_3)_2$], 18.3 [$C(CH_3)_3$], 25.5, 27.5 [$C(CH_3)_2$], 25.9 [$C(CH_3)_3$], 27.4 (C-1), 41.6

(C-2), 63.6 (C-5′), 78.5 (C-5), 81.3 (C-4), 81.9 (C-3′), 83.3, 84.5, 84.7 (C-1′,2′,4′), 114.0 [*C*(CH_3)$_2$], 186.3 (C-3).

Anal. Calcd for $C_{19}H_{32}O_5Si$ (368.54): C, 61.92; H, 8.75. Found: C, 62.21; H, 8.93.

1-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)pent-4-yn-3-one (28)

Method A. Purified by flash chromatography (solvent A_7).

Yield: 266 mg (54%); colorless syrup; $[\alpha]_D^{22}$ –5.6 (*c* 1.2, CH_2Cl_2); R_f = 0.52 (solvent A_2).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.06 [s, 9 H, C(CH_3)$_3$], 1.34, 1.53 [s, 6 H, C(CH_3)$_2$], 1.82–2.12 (m, 2 H, H-1), 2.75 (m, 2 H, H-2), 3.77 (m, 1 H, H-5′), 3.85 (app dt, $^3J_{1a,1'}$ = 8.3 Hz, $^3J_{1b,1'} \approx {}^3J_{1',2'}$ = 5.1 Hz, 1 H, H-1′), 4.03 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.7 Hz, 1 H, H-4′), 4.30 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.1 Hz, 1 H, H-2′), 4.71 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.7 Hz, 1 H, H-3′), 7.33–7.45, 7.64–7.71 (2 × m, 10 H, Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.2 [*C*(CH_3)$_3$], 25.5, 27.5 [C(*C*H_3)$_2$], 26.8 [C(*C*H_3)$_3$], 27.5 (C-1), 41.7 (C-2), 64.1 (C-5′), 78.6 (C-5), 81.3 (C-4), 81.8 (C-3′), 83.1, 84.2, 84.7 (C-1′,2′,4′), 114.2 [*C*(CH_3)$_2$], 127.7, 127.7, 135.6, 135.6 (*o*-, *m*-Ph), 129.7 (*p*-C_6H_5), 133.2, 133.3 (*i*-Ph), 186.3 (C-3).

MS (CI): *m*/*z* (%) = 493 (3) $[M + H]^+$.

Anal. Calcd for $C_{29}H_{36}O_5Si$ (492.68): C, 70.70; H, 7.37. Found: C, 70.68; H, 7.42.

1-(5-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)-5-phenyl-pent-4-yn-3-one (29)

Method B. Purified by flash chromatography (solvent A_{10}).

Yield: 4.0 g (90%); pale-yellow syrup; $[\alpha]_D^{23}$ –28.0 (*c* 1.0, CH_2Cl_2); R_f = 0.39 (solvent A_6).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.06, 0.07 [2 × s, 6 H, Si(CH_3)$_2$], 0.89 [s, 9 H, C(CH_3)$_3$], 1.34, 1.52 [2 × s, 6 H, C(CH_3)$_2$], 1.89–2.12 (m, 2 H, H-1), 2.72–2.91 (m, 2 H, H-2), 3.71 (m, 2 H, H-5′), 3.91 (app dt, $^3J_{1a,1'}$ = 8.0 Hz, $^3J_{1b,1'} \approx {}^3J_{1',2'}$ = 5.0 Hz, 1 H, H-1′), 4.01 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.5 Hz, 1 H, H-4′), 4.31 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{1',2'}$ = 5.0 Hz, 1 H, H-2′), 4.64 (dd, $^3J_{2',3'}$ = 6.6 Hz, $^3J_{3',4'}$ = 3.5 Hz, 1 H, H-3′), 7.34–7.48 (m, 3 H, *m*-, *p*-Ph), 7.55–7.58 (m, 2 H, *o*-Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –5.4, –5.3 [Si(CH_3)$_2$], 18.3 [*C*(CH_3)$_3$], 25.5, 27.5 [C(*C*H_3)$_2$], 25.9 [C(*C*H_3)$_3$], 27.8 (C-1), 41.6 (C-2), 63.6 (C-5′), 81.9 (C-3′), 83.4, 84.5, 84.8 (C-1′,2′,4′), 87.7 (C-4), 90.7 (C-5), 114.0 [*C*(CH_3)$_2$], 120.0 (*i*-Ph), 128.6 (*m*-Ph), 130.6 (*p*-Ph), 133.0 (*o*-Ph), 186.9 (C-3).

Anal. Calcd for $C_{25}H_{36}O_5Si$ (444.64): C, 67.53; H, 8.16. Found: C, 67.62; H, 8.30.

1-(5-*O*-*tert*-Butyldiphenylsilyl-2,3-*O*-isopropylidene-1-deoxy-β-D-ribofuranos-1-yl)-5-phenyl-pent-4-yn-3-one (30)

Method A. Purified by flash chromatography (solvent A_{10}).

Yield: 284 mg (54%); colorless crystals; mp 48–50 °C (EtOAc–hexane); $[\alpha]_D^{23}$ –6.9 (*c* 1.0, CH_2Cl_2); R_f = 0.55 (solvent A_2).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.06 [s, 9 H, C(CH_3)$_3$], 1.34, 1.52 [2 × s, 6 H, C(CH_3)$_2$], 1.89–2.18 (m, 2 H, H-1), 2.84 (m, 2 H, H-2), 3.79 (m, H-5′), 3.91 (app dt, $^3J_{1a,1'}$ = 8.2 Hz, $^3J_{1b,1'} \approx {}^3J_{1',2'}$ = 5.1 Hz, 1 H, H-1′), 4.04 (app q, $^3J_{3',4'} \approx {}^3J_{4',5'}$ = 3.7 Hz, 1 H, H-4′), 4.34 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{1',2'}$ = 5.1 Hz, 1 H, H-2′), 4.73 (dd, $^3J_{2',3'}$ = 6.7 Hz, $^3J_{3',4'}$ = 3.7 Hz, 1 H, H-3′), 7.33–7.46 (m, 9 H), 7.52–7.56 (m, 2 H), 7.65–7.72 (m, 4 H, Ph).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.2 [*C*(CH_3)$_3$], 25.6, 27.5 [C(*C*H_3)$_2$], 26.8 [C(*C*H_3)$_3$], 27.8 (C-1), 41.7 (C-2), 64.1 (C-5′), 81.8 (C-3′), 83.2, 84.2, 84.7 (C-1′,2′,4′), 87.7 (C-4), 90.9 (C-5), 114.2 [*C*(CH_3)$_2$], 119.9 (*i*-$Ph_{C\equiv C}$), 127.7, 127.7, 128.6, 133.0, 135.6, 135.6 (*o*-, *m*-Ph), 129.7, 129.7, 130.7 (*p*-Ph), 133.2, 133.3 (*i*-Ph), 186.9 (C-3).

MS (CI): *m*/*z* (%) = 569 (7) $[M + H]^+$.

Anal. Calcd for $C_{35}H_{40}O_5Si$ (568.77): C, 73.91; H, 7.09. Found: C, 73.63; H, 7.16.

1-[3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-1,2-dideoxy-β-D-ribofuranos-1-yl]pent-4-yn-3-one (33)

Method B. Reaction time 1 h; purified by flash chromatography (solvent A_7).

Yield: 3.5 g (77%); colorless syrup; $[\alpha]_D^{24}$ –26.5 (*c* 1.0, CH_2Cl_2); R_f = 0.47 (solvent A_6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.98–1.09 [m, 28 H, C*H*(CH_3)$_2$], 1.72–2.09 (m, 4 H, H-1,2′), 2.71 (m, 2 H, H-2), 3.21 (s, 1 H, H-5), 3.65–3.76 (m, 2 H, H-4′,5′a), 3.95–4.16 (m, 2 H, H-1′,5′b), 4.36 (app dt, $^3J_{2'a,3'} \approx {}^3J_{3',4'}$ = 7.9 Hz, $^3J_{2'b,3'}$ = 4.5 Hz, 1 H, H-3′).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.5, 12.9, 13.3, 13.5 [*C*H(CH_3)$_2$], 16.9, 17.0, 17.1, 17.3, 17.4 (2), 17.4, 17.5 [CH(*C*H_3)$_2$], 29.2 (C-1), 40.2 (C-2′), 41.8 (C-2), 63.7 (C-5′), 73.5 (C-3′), 76.2 (C-1′), 78.5 (C-5), 81.3 (C-4), 86.0 (C-4′), 186.6 (C-3).

Anal. Calcd For $C_{23}H_{42}O_5Si_2$ (454.75): C, 60.75; H, 9.31. Found: C, 60.38; H, 9.24.

1-[3,5-*O*-(Tetraisopropyldisiloxane-1,3-diyl)-1,2-dideoxy-β-D-ribofuranos-1-yl]-5-phenylpent-4-yn-3-one (34)

Method B. Reaction time ca. 2 h; purified by flash chromatography (solvent A_9).

Yield: 3.1 g (60%); pale-yellow syrup; $[\alpha]_D^{22}$ –27.6 (*c* 1.0, CH_2Cl_2); R_f = 0.50 (solvent A_6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.98–1.11 [m, 28 H, C*H*(CH_3)$_2$], 1.75–2.12 (m, 4 H, H-1,2′), 2.80 (m, 2 H, H-2), 3.73 (m, 2 H, H-4′,5′a), 4.02 (dd, $^2J_{5'a,5'b}$ = 15.1 Hz, $^3J_{4',5'b}$ = 7.2 Hz, 1 H, H-5′b), 4.10 (m, 1 H, H-1′), 4.38 (app dt, $^3J_{2'a,3'} \approx {}^3J_{3',4'}$ = 7.9 Hz, $^3J_{2'b,3'}$ = 4.5 Hz, 1 H, H-3′), 7.34–7.49 (m, 3 H), 7.35–7.59 (m, 2 H, Ph).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.5, 12.9, 13.4, 13.5 [*C*H(CH_3)$_2$], 16.9, 17.0, 17.1, 17.3, 17.4, 17.4 (2), 17.5 [CH(*C*H_3)$_2$], 29.6 (C-1), 40.3 (C-2′), 41.8 (C-2), 63.8 (C-5′), 73.6 (C-3′), 76.5 (C-1′), 86.0 (C-4′), 87.7 (C-4), 90.8 (C-5), 120.0 (*i*-Ph), 128.6, 133.0 (*o*-, *m*-Ph), 130.7 (*p*-Ph), 187.2 (C-3).

MS (ESI): *m*/*z* (%) = 517 (100) $[M + H]^+$.

Anal. Calcd for $C_{28}H_{44}O_5Si_2$ (516.82): C, 65.07; H, 8.58. Found: C, 65.14; H, 8.53.

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